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The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. | Patent application No. | Demande de brevet n°

02078110.0

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk

PRIORITY DOCUMENT
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Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se referer à la description.)

Plasma nitriding of maraging steel, shaver cap for an electric shaver, cutting device made out of such steel and an electric shaver

In Anspruch genommene Prioriät(en) / Priority(ies) claimed /Priorité(s) revendiquée(s)
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C23C4/00

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AT BE BG CH CY CZ DE DK EE ES FI FR GB GR IE IT LI LU MC NL PT SE SK TR

Plasma nitriding of maraging steel, shaver cap for an electric shaver, cutting device made out of such steel and an electric shaver

The invention relates to a method for the plasma nitriding of precipitation hardenable stainless steels or stainless maraging steels. The invention also relates to a shaver cap and a cutting device. The invention further relates to an electric shaver.

For years, maraging steels have been used in industry for applications where hardened steel was necessary. Old established methods for hardening steel, some dating back thousands of years such as heating and quenching, have been supplemented by more advanced methods, such as plasma nitriding, whereby nitrogen is included in the structure of the metal. This alteration of the structure of the metal yields a thin layer of hardened metal on the outside of the steel item, making it much more wear resistant.

Given the many useful qualities of stainless steels, these have found wide application in all kinds of fields. Hardness however is not a particular strong point of stainless steel. Hardening stainless steel is compromised because of unwanted reactions, that although they make the steel harder they also reduce its corrosion resistance.

To date maraging steel has mostly been employed in situations where hardness was a prime factor, but the corrosion resistance of maraging steels leaves room for improvement. A recent example of the dilemma between hardness and corrosion resistance proved to be the Coolskin Philishave®. This is an electric shaver that can be used for wet shaving, and was developed to combine the advantages of wet shaving with a razor with the safety features of an electric shaver. The shaver uses a shaver head with an outer blade made of very thin steel. Since introduction of the Coolskin Philishave® there is a problem in that the outer blade wears too fast. Because of the required hardness this blade is made of maraging steel, for want of a sufficiently hard stainless steel alternative but still this proves to be insufficiently hardwearing. At the same time it has become clear that improved corrosion resistance is also desired.

Further hardening of maraging steel according to the present state of the art has the disadvantage that although the hardness can be increased the toughness decreases accordingly. In other words hardened steel becomes brittle, making it unsuitable for certain purposes. It can be imagined that this problem is less acute in say ball bearings where the hardened surfaces are inflexible than in a shaver blade which is very thin (order of magnitude

of 70μm) and flexible. With increased hardening the corrosion resistance of the maraging steel is impaired.

Steel exists in various crystalline states, that is to say the atoms can be arranged in different configurations. Also the addition of other elements can alter the atomic configuration of steel, and thereby its characteristics. Stainless steel for instance is an alloy of steel with up to 18% Chromium and around 11% Nickel, giving this steel its stainless corrosion resistant properties. Steel itself is made harder than pure iron because it contains carbon. The main states of the steel of interest for the present invention are martensite and austenite. Of these, austenite is the softer, more deformable state. In general it can be said that items are shaped with the metal in the austenitic state and subsequently hardened by heating to transform the metal at least partly in the martensitic state. Traditionally, in order to maintain the martensitic state at a lower temperature the steel is quenched, i.e. rapidly cooled off. Another widely used method is precipitation hardening.

Several solutions have been proposed in the art to the problem of improving the hardness of certain stainless steels and non stainless maraging steels. EP 1 008 659 discloses a method for the production of steel plates from a specific type of martensite hardening steel. The method disclosed teaches that the age hardening temperatures have to stay below the martensite / austenite transition temperature and that also the surface hardening is realised at a temperatures below the martensite / austenite transition temperature. A drawback of the method known in the art is that this method can only be applied to iron-nickel-cobalt maraging steel, which is not corrosion resistant.

The object of the invention is to provide a type of steel that is both very hard and very well corrosion resistant, while maintaining sufficient tensile strength.

To achieve this object the invention provides a method for the plasma nitriding of precipitation hardenable steels or maraging steels, characterised in that the maraging steel is a stainless maraging steel and the plasma nitriding is carried out at a temperature below 500°Celcius. The resulting hardness that can be reached with the method according the invention is in excess of 1400 HV. Also the Young modulus in the compound layer increases with 20 % to 25 % compared to the base material. The method according to the invention can be applied to already hardened, maraging stainless steel and precipitation hardenable stainless

steel or to simultaneously precipitation-harden and plasma nitride the steels. As the closed prior art discloses a method for the production of steel plates the present invention can be used for the production of all kinds of products, especially products precisely dimensioned. These products can be produced in the required dimensions before applying the method according the invention, providing the advantage that also smaller machine parts, like parts of shaver heads or cutting tools, can be produced as very hard and very well corrosion resistant element, in combination with sufficient toughness.

EP 1 094 127 proposes plasma nitriding of maraging steel at a temperature between 450 and 530 °Celcius. This temperature range corresponds with the transition temperature between martensite and austenite, depending on the composition of the steel. At this temperature steel can be hardened by precipitation hardening. However there is no lead in this document that the technique could also be useful to apply for stainless steel. US 6,033,496 describes the combined precipitation hardening and nitriding of maraging steel, this indicates that both processes are carried out simultaneously. US 5,953,966 teaches plasma nitriding at a temperature below the austenite martensite transition temperature. This document is directed on screwdriver bits, for which a hardness of up to 3.000 HV is obtained. It does however not teach the use of this process for stainless steels. US 5,503,687 teaches the use of solution nitriding of stainless steel at temperatures of between 1000 and 1200 °Celcius. Lastly US 6,007,871 teaches the use of plasma nitriding of chrome containing steel at 500 °Celcius, but combines the technique with adding a layer of titanium nitride for further hardness.

The methods according the prior art present several problems for the production of delicate items, like for instance the above mentioned shaver blade. Treatment at high temperatures can lead to spatial distortions of the product. Also the formation of chromium compositions, notably chromium nitride adversely affect the corrosion resistance. But, most important, none of the methods proposed for stainless steels yield sufficient hardness.

Preferably the plasma nitriding is carried out simultaneously with or consecutively to, precipitation hardening. The combination of nitriding and precipitation hardening is evident this leads to a less complex processing route.

The temperature at which the plasma nitriding and precipitation hardening are carried out ranges from 300 °C to 500 °C, preferably from 370 to 380° Celsius, more preferably 375° Celsius, depending on the composition of the material involved, but never exceeds 500 °Celcius. The duration of the plasma nitriding method according to the invention

depends on the desired thickness of the hardened layer and the temperature used. For instance plasma nitriding at 500 °C for 2 hours gives 22 μm layer thickness, at 450 °C for 5 hours gives 17 μm layer thickness and at 375 °C for 20 hours gives 8 μm layer thickness. The plasma nitriding according to the invention is otherwise carried out according to the state of the art and uses pulsed plasma mode and nitrogen as a nitrogen source. The resulting hardness is can be 1500 HV, an remarkable value in view of the prior art, notably US 6,007,871.

The method according to the present invention can be applied to produce any steel item that is required to be both very well corrosion resistant and hard-wearing. The method according to the present invention is particularly suitable for items that are thin and/ or of intricate shape, and demand high tensile strength. Examples of such items are, but not limited to, shaver blades, razors, cutting tools, rotating knives e.g. in kitchen equipment, automotive parts.

The invention also relates to a shaver cap for an electric shaver made of maraging or precipitation hardenable stainless steel, characterised in that the maraging steel or stainless steel shaver cap is plasma nitrided at a temperature below 500° Celsius. Advantages of said stainless steel are already described above.

The invention also relates to a cutting device made of maraging or precipitation hardenable stainless steel, characterised in that the maraging steel or stainless steel is plasma nitrided at a temperature below 500° Celsius. With a cutting device or cutting element is meant an individual working shaver blade or a shaver blade that works in cooperation with another shaver blade. Such a construction of cooperating shaver blades can for instance be found in a shaver with an internal rotating cutting element that is surrounded by an external counter cutting element (cap) that has a stationary position. Both the internal rotating cutting element and the external stationary counter cutting element are referred to in this document as cutting elements.

The invention further relates to an electric shaver comprising at least one of such a cutting element.

The present invention can be further illustrate by means of several non-limitative examples given below.

Example 1

Manufacture of a shaving cap according to the invention out of Sandvik 1RK91 stainless maraging steel with plasma nitriding and ageing combined in one process step.

A shaving head is stamped out of strip material and by heat treatment the microstructure is transformed for 70 % into martensite with a resulting hardness of 300 HV. The shaving head is machined into its final shape with slots and holes. After this the shaving head is treated in a pulsed plasma nitriding furnace at 375 °C for 20 hour between 300 and 475 Pa nitrogen pressure. While the shaving head is being nitrided at the same time the precipitation hardening (ageing) takes place. With an average thickness of the lamellae of around 70 μm this results in a compound layer of 10 to 20 μm. This is illustrated in the cross section of a hardened lamellae in figure 1. In remaining base material enveloped by the compound layer the hardness is increased by precipitation hardening (ageing) to 500 HV. In the compound layer via the combination of precipitation hardening (ageing) and nitriding the hardness reaches 1500 HV.

Example 2

Manufacture of a cutting device according to the invention out of Sandvik 1RK91 stainless maraging steel or Carpenter Custom 465 stainless maraging steel with plasma nitriding and ageing combined in one process step.

A rotary shaver cutter is stamped and formed out of 0.30 mm thick cold rolled strip material with an as received microstructure containing about 80 % martensite and a hardness of more than 325 HV. The cutter legs are made flat and sharpened by spark erosion. After this the shaving head is treated in a pulsed plasma nitriding furnace at 375 °C for 20 hour between 300 and 475 Pa nitrogen pressure. While the rotary cutter shaving head is being nitrided at the same time the precipitation hardening (ageing) takes place. A compound layer of 10 to 20 μm is formed into the all surfaces of the cutter. In remaining base material enveloped by the compound layer the hardness is increased by precipitation hardening (ageing) to 500 HV or higher. In the compound layer via the combination of precipitation hardening (ageing) and nitriding the hardness reaches 1500 HV.

CLAIMS:

1. Method for the plasma nitriding of precipitation hardenable stainless steels or maraging steels, characterised in that the maraging steel is a stainless maraging steel and the plasma nitriding is carried out at a temperature below 500°Celcius.

2. Method according claim 1, characterised in that stainless steel products, like shaver parts, machine parts, and cutting tools, can be produced in required dimensions, before the plasma nitriding is carried out.

3. Method according to claim 1 or 2, characterised in that the plasma nitriding is carried out simultaneously with or consecutively to, precipitation hardening.

4. Method according to any of the foregoing claims, characterised in that the plasma nitriding and/or precipitation hardening is carried out at a temperature chosen between 300° and 500° Celsius, preferably from 370 to 380° Celsius, more preferably 375° Celsius.

5. Shaver cap for an electric shaver, made of maraging or precipitation hardenable stainless steel, characterised in that the maraging steel or stainless steel shaver cap is plasma nitrided at a temperature below 500 °Celcius.

6. Cutting device made of maraging or precipitation hardenable stainless steel, characterised in that that the maraging steel or stainless steel is plasma nitrided at a temperature below 500 °Celcius.

7. Electric shaver comprising at least one of the cutting elements according any of the claims 1 – 6.

ABSTRACT:

The invention relates to a method for the plasma nitriding of precipitation hardenable stainless steels or stainless maraging steels. The invention also relates to a shaver cap for an electric shaver. The invention also relates to a cutting device. The invention further relates to an electric shaver comprising at least one of such a cutting device.

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INTERNATIONAL SEARCH REPORT

International Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C23C8/38 C23C8/26 C21D6/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C23C C21D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 536 549 A (NELSON CARL W ET AL) 16 July 1996 (1996-07-16)	1-4
Y	column 2, line 19 - line 24 column 4, line 27 - line 34 column 10, line 1 - line 8 claims 1,5,6 ---	5-7
Y	EP 0 743 144 A (MATSUSHITA ELECTRIC WORKS LTD) 20 November 1996 (1996-11-20)	5-7
A	page 2, line 5 - line 48 page 3, line 19 - line 48 page 4, line 4 - line 31 examples 11,12 figures 1-3,5,6 claims 1,3,5,6 ---	1-4

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 May 2004	01/06/2004

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Ovejero, E

INTERNATIONAL SEARCH REPORT

International Application No
IB 03/03190

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 010, no. 004 (C-322), 9 January 1986 (1986-01-09) & JP 60 162766 A (KIYUUSHIYUU HITACHI MAKUSERU KK), 24 August 1985 (1985-08-24) abstract ---	6,7
A	US 6 238 490 B1 (BELL THOMAS ET AL) 29 May 2001 (2001-05-29) column 1, line 47 - line 51 column 2, line 54 - line 65 claims 1-4,10 ---	1-4
A	EP 1 091 006 A (HITACHI METALS LTD) 11 April 2001 (2001-04-11) page 4, paragraph 20 - paragraph 22 page 6, paragraph 44 - paragraph 45 claims 1,8; table 1 ---	1-4
A	EP 1 008 659 A (DER DILLINGER HUETTENWERKE AG) 14 June 2000 (2000-06-14) claims 1-5 -----	1-7

INTERNATIONAL SEARCH REPORT

International Application No
PCT/IB 03/03190

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